

Concurrent CO₂ Control and O₂ Generation for Advanced Life Support

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ABSTRACT

The electrochemical reduction of carbon dioxide (CO₂) using ceramic oxygen generators (COGs) is well known and widely studied, however, conventional devices using yttria-stabilized zirconia (YSZ) electrolytes operate at temperatures greater than 700 °C. Operating at such high temperatures increases system mass compared to lower temperature systems because of increased energy overhead to get the COG up to operating temperature and the need for heavier insulation and/or heat exchangers to reduce the COG oxygen (O₂) output temperature for comfortable inhalation.

Recently, the University of Florida developed novel ceramic oxygen generators employing a bilayer electrolyte of gadolinia-doped ceria and erbia-stabilized bismuth for NASA's future exploration of Mars. To reduce landed mass and operation expenditures during the mission, *in-situ* resource utilization was proposed using these COGs to obtain both life-supporting oxygen and oxidant/propellant fuel, by converting CO₂ from the Mars atmosphere. The results showed that oxygen could be reliably produced from CO₂ at temperatures as low as 400°C. These results indicate that this technology could be adapted to CO₂ removal from a spacesuit and other applications in which CO₂ removal was an issue.

The strategy proposed for CO₂ removal for advanced life support systems employs a catalytic layer combined with a COG so that it is reduced all the way to solid carbon and oxygen.

Hence, a three-phased approach was used for the development of a viable low weight COG for CO₂ removal. First, to reduce the COG operating temperature a high oxide ion conductivity electrolyte was developed. Second, to promote full CO₂ reduction while avoiding the problem of carbon deposition on the COG cathode, novel cathodes and a removable catalytic carbon deposition layer were designed. Third, to improve efficiency, a pre-stage for CO₂ absorption was used to concentrate CO₂ from the exhalate before sending it to the COG. These subsystems were then integrated into a single CO₂ removal system. This paper describes our progress to date on these tasks.

INTRODUCTION

Weight is one of the most crucial factors in determining the viability of manned space travel, such as a mission to Mars. Ostensibly, much of the technology needed for manned space travel is already in place but its weight is prohibitive. Particularly, life support related technologies are currently too heavy for an astronaut to carry for a reasonable duration without exhaustion. In this work we focus on two crucial parts of the life support system: CO₂ removal from spacesuits and oxygen (O₂) supply for breathing. Current CO₂ removal technologies are not suitable for use on a Mars mission because of their weight and/or interaction with the Martian environment. For example, current CO₂ removal systems employing lithium hydroxide canisters, would require approximately sixty pounds of consumable lithium hydroxide (LiOH) for a proposed five day Mars surface mission. To decrease weight penalties on a mission to Mars, it is therefore imperative to move away from such systems. Cycling bed and permeable membranes systems are also unsuitable because the high CO₂ concentration in the Martian atmosphere precludes simply venting the CO₂ after its removal from a spacesuit. Finally, none of these technologies capitalize on the presence of vital O₂ bound up in the CO₂ molecule. Hence, new methods must be developed or older/existing alternatives must be perfected to remove CO₂ from the space suit, without the need for venting, and to recover the oxygen from the CO₂ molecule. Indeed, as we will detail below, if a system was able to capture and recycle all the oxygen from the exhaled CO₂ it may be possible to considerably reduce the need for additional O₂ sources and hence gain significant weight savings.

We recently investigated ceramic oxygen generators (COGs) for NASA's future manned exploration of Mars [1, 2]. To reduce landed mass, *in-situ* resource utilization (ISRU) was proposed for obtaining both life-supporting oxygen and oxidant/propellant fuel, by converting CO₂ from the Mars atmosphere. To this end, we developed (NASA contract #NAG 10-303) a novel COG employing a bilayer electrolyte of gadolinia-doped ceria and erbia-stabilized bismuth oxide for ISRU. Our results showed that oxygen could be reliably produced from CO₂ at temperatures as low as 400 °C without degradation in power.

The strategy for CO₂ removal from a spacesuit to be used in a Mars mission is simple in concept. CO₂ will be removed using a catalytic layer in series with a ceramic oxygen generator (COG) so that it is reduced to carbon and oxygen as described below:



Carbon dioxide is electro-catalytically reduced at the cathode of a COG which transports the oxygen (as O²⁻ ions) away leaving behind solid carbon. The driving force is an electric potential applied across a dense oxide ion-conducting electrolyte, as shown in Figure 1. Under the influence of this potential, CO₂, adsorbed on the cathode, releases oxygen species, which are then incorporated into the lattice of the electrolyte as oxide ions and transported to the anode where they recombine to form O₂ molecules. The oxygen flux is given by Faradays equation:

$$J_{\text{O}_2} = i_{\text{app}} n^{-1} F^{-1} = \dot{W} V_{\text{app}}^{-1} n^{-1} F^{-1} \quad (2)$$

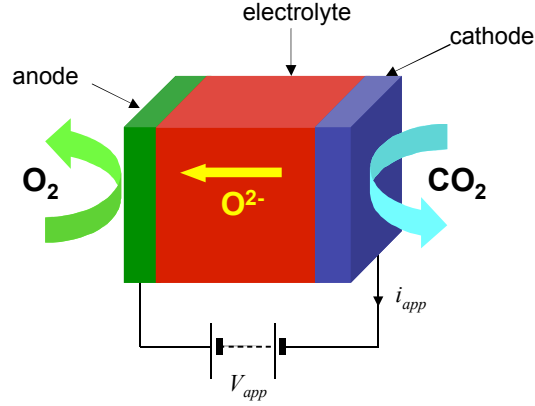


Figure 1. Conceptual representation of a ceramic oxygen generator (COG).

where J_{O_2} is the molar flux of oxygen (mol/s), i_{app} is the applied current (A), \dot{W}_{app} is the applied power, V_{app} is the applied voltage, F is Faraday's constant and n is the number of electrons transferred in the ionization of an oxygen molecule.

The electrochemical reduction of CO_2 is well known and widely studied [1-4]. However, conventional devices using yttria-stabilized zirconia (YSZ) electrolytes operate at temperatures greater than 700 °C. Such high temperature operation increases mass versus lower temperature systems because of increased energy overhead to get the COG up to operating temperature and, especially, the need for heavier insulation and/or heat exchangers to reduce the COG O_2 output temperature for comfortable inhalation. Furthermore, most of the research using COGs has concentrated on partial reduction of CO_2 to CO. Partial reduction is typically preferred for COGs to avoid “coking” of the cathode which can severely attenuate COG efficiency. However, for a spacesuit this is undesirable, because carbon monoxide CO is extremely toxic for humans and recovering only 50% of the potentially available oxygen is an expense to be avoided if possible.

From thermodynamics, complete reduction of CO_2 , Equation (1), requires ~ 1.1 V/mole (from 500 °C to 700 °C). Therefore, given that CO_2 is produced metabolically at the rate of 25 mg/s (0.00057 mol/s), then, from Equation (2), complete reduction of CO_2 (or equivalently removal of all the oxygen released in the reaction) would, theoretically, require a power consumption of ~ 240 W. For a more realistic value, however, the operational losses (due to Ohmic resistances and electrode overpotentials) must be included and, for accuracy, these values must be obtained from experiment. Furthermore, careful system design may allow for a reduction in the required oxygen removal rate and hence the applied power required.

In summary, to make this technology more suitable for advanced life support systems, it will be necessary to (1) reduce the operating temperature, in order to reduce the mass and energy overhead for COG operation; (2) fully reduce CO_2 to carbon and oxygen, while avoiding cathode “coking”; and (3) concentrate CO_2 so that the COG does not pump O_2 directly from the exhalate.

TECHNICAL APPROACH

A three-pronged approach was used for the development of a viable low weight COG for CO_2 removal in an advanced life support system. First, a novel high oxide ion conductivity

electrolyte was used to lower the operating temperature. Second, to promote full CO₂ reduction while avoiding the problem of “coking”, a removable catalytic carbon deposition layer (CCDL) was designed. Third, to improve efficiency, a pre-stage for CO₂ absorption was designed to concentrate CO₂ from the exhalate before sending it to the COG. These three facets will be integrated into a CO₂ removal system for advanced life support.

System Design

The CO₂ removal system has two stages, as shown schematically in Figure 2 and prototypically in Figure 3. Stage 1 is based on a system we patented for NO_x removal [5] and its purpose is to concentrate the CO₂ before it is released to the COG. Thus, the amount of oxygen pumped through the COG is limited to that liberated in the reduction of the CO₂. Thereby, the power consumption of the COG is considerably reduced. Figure 2a shows how the CO₂ (initial) removal and concentration is achieved. First, exhalate from the spacesuit is piped through one of two chambers, each containing a sorbent bed to remove CO₂ from the exhalate. By closing the valves v_1 and v_2 while opening the valves v_3 and v_4 , the top chamber is excluded from the *ventilation loop*. Hence CO₂ is removed from the exhalate stream by the bottom chamber only.

The saturation level of the sorbent bed in the lower chamber can be monitored by using a CO₂ sensor, s_2 , to measure CO₂ concentration in the effluent. Once sensor s_2 indicates that the CO₂ concentration has attained a predetermined value, the top chamber is automatically switched into the *ventilation loop* by opening v_1 and v_2 . Simultaneously, the lower chamber is switched out of the *ventilation loop* and connected to the COG by closing v_3 and v_4 . Hence CO₂ removal is now handled by the top chamber. At this time, CO₂ previously absorbed and concentrated in the lower chamber is now desorbed and flows to the COG (stage 2) where it is reduced to carbon and O₂. The O₂ recovered by the COG can then be reintroduced to the *ventilation loop* as needed. When the CO₂ sensor s_1 indicates that the CO₂ concentration has attained a predetermined value, the chambers are cycled into and out of the ventilation loop again so that the top chamber can release its CO₂ to the COG while the lower chamber removes CO₂ from the exhalate.

Stage 2, Figure 2b, is the COG. The COG consists of a chamber housing individual planar or tubular electrochemical cells, a removable CCDL and its support. Each electrochemical cell is oriented so that the cathode side is inside the chamber and the anode side is on the outside of the compartment. A gas-tight seal is built into the chamber wall to isolate the cathode from the anode side of the COG. This allows the oxygen produced at the anode to be readily collected and reintroduced to the *ventilation loop*. When carbon buildup surpasses an experimentally predetermined level, the removable CCDL can be replaced with another one. The carbon deposits may then be disposed of or reused.

It is important, therefore, to employ an adsorbent material that does not have to be replaced during an eight hour period and a CCDL that at the most must be replaced once during an eight hour period. As a safety measure a carbon monoxide (CO) sensor such as one we developed earlier for NASA, would be included to monitor CO levels in the chamber [6]. This parts per billion CO sensor measures even tiny concentrations of CO and thus would be able to indicate whether CO₂ was only being partially reduced in the COG. CO formation can result from carbon accumulation on the CCDL and so may indicate the need to replace it. CO formation also results in a reduction of the oxygen being recovered by the COG for reintroduction to the ventilation loop.

This design has the potential to significantly reduce the mass of the oxygen carried in the tank of the spacesuit since the oxygen used by the human is continuously regenerated. The COG essentially removes carbon from the loop. The carbon, deposited on the removable CCDL, can then be discarded or re-used for another process. Indeed, if the system were to achieve 100% efficiency no additional O_2 source (such as oxygen tanks) would be necessary as all of the astronaut's exhaled CO_2 would be converted to O_2 for continuous life support.

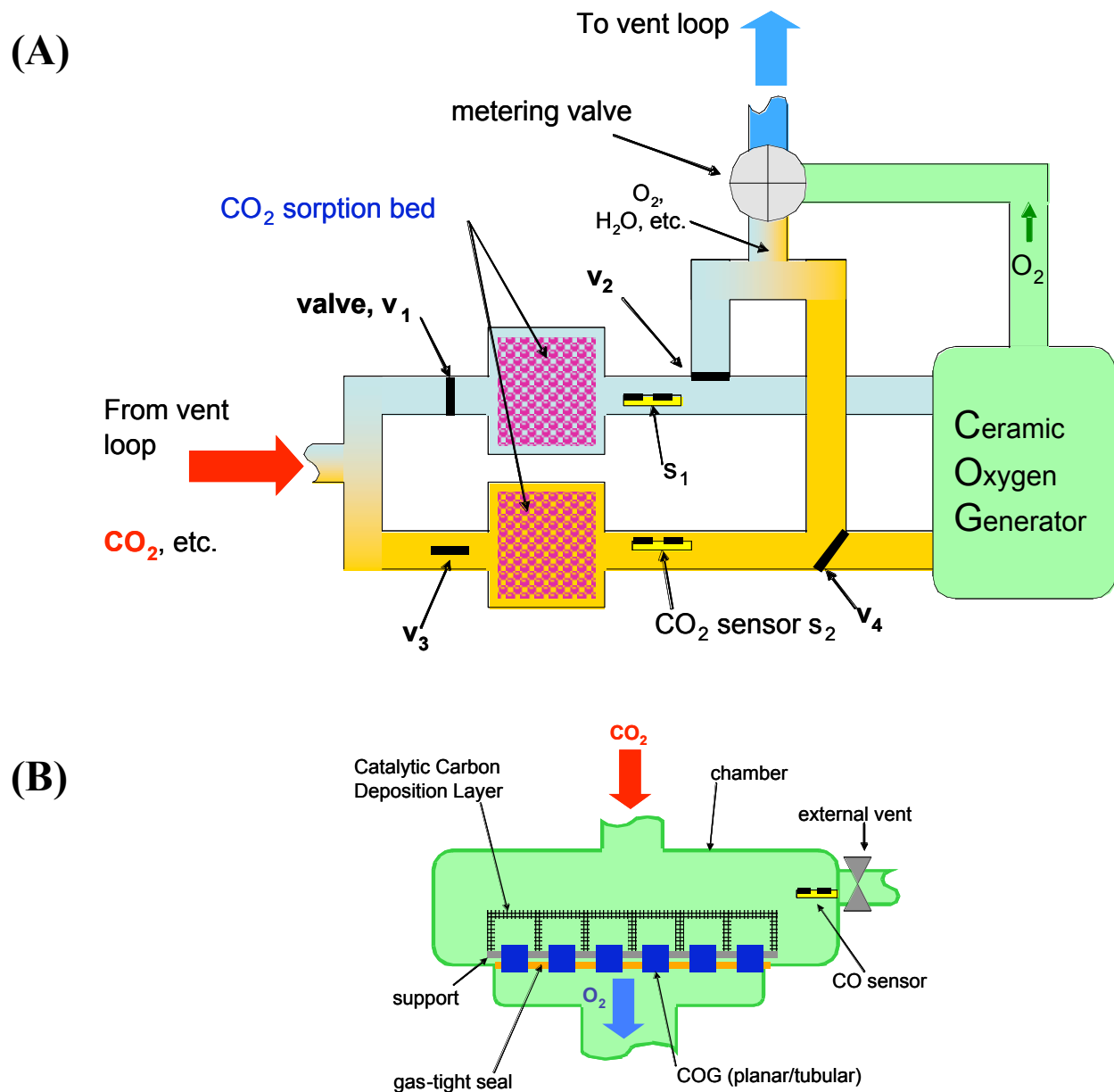


Figure 2. CO_2 removal system (a) Stage 1: CO_2 removal from the ventilation loop; (b) Stage 2: CO_2 decomposition in the COG.

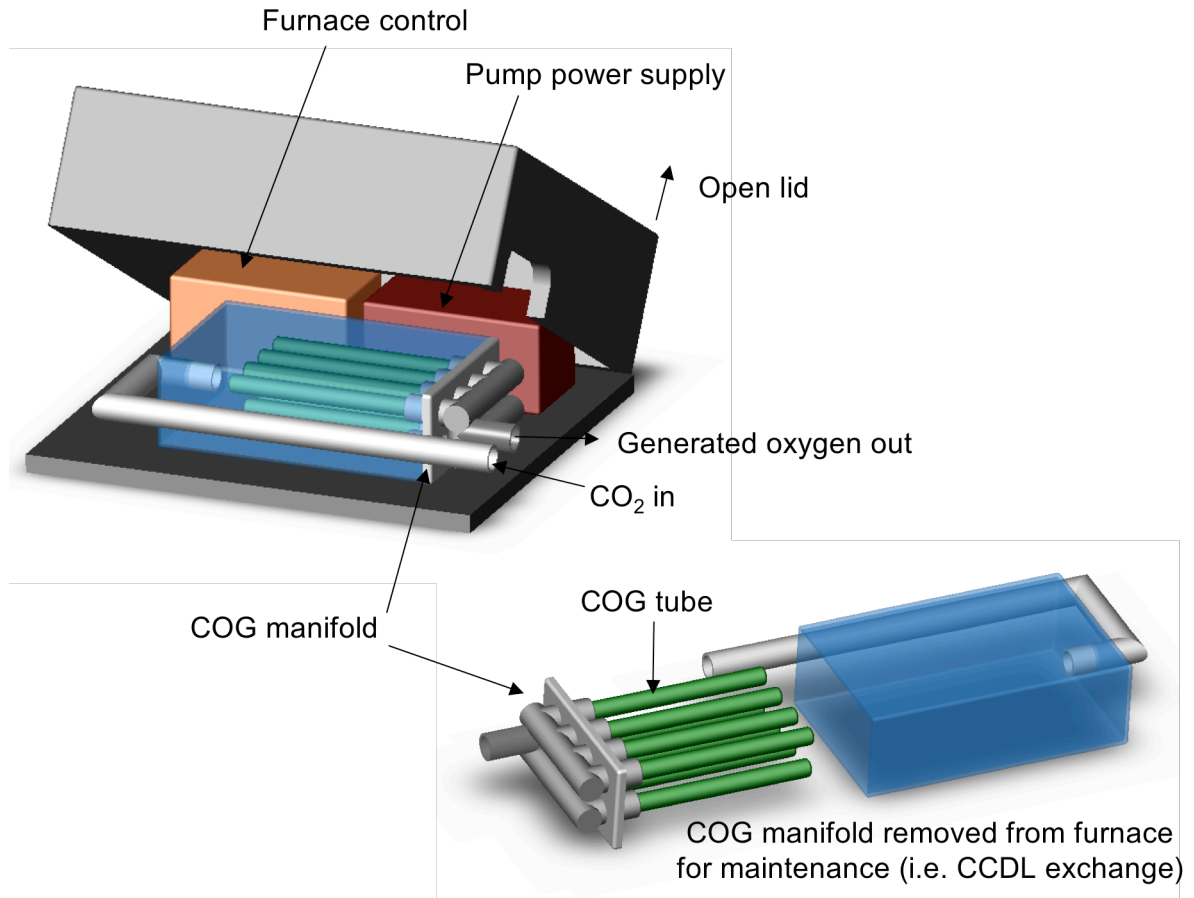


Figure 3. Generator for Advanced Life Support Advanced Life Support System.

CO₂ Sorbent System

Selecting an efficient CO₂ sorbent for the system, Figure 2a, is crucial, since this adsorbent will not only add weight to the system but also increase the energy demand (heating) of the system. Therefore, it is necessary to find an adsorbent that is very efficient per unit mass and an adsorbent system with a low thermal regeneration requirement. Existing state-of-the-art CO₂ sorbents developed by NASA will be used for this component of the life support system.

Catalytic Carbon Deposition Layer and Electrode Design

Electrode design is a critical factor for a COG oxygen removal system geared for full reduction of CO₂ to carbon and oxygen. As mentioned above, full CO₂ reduction will result in carbon buildup on the cathode surface. Above a critical level the carbon deposits could (i) block gas diffusion paths through the cathode to the triple-phase boundaries (TPBs)—i.e., lines where cathode, electrolyte and gas phase coincide; and (ii) reduce TPB length. As the gas diffusion paths become clogged, concentration overpotential increases until COG operation ceases due to *starvation*. Similarly, as TPB length decreases activation overpotential increases until COG operation ceases due to the absence of oxygen incorporation sites on the electrolyte surface.

To overcome this we will employ a removable catalytic carbon deposition layer above the cathode to precipitate carbon before it reaches the cathode. Nickel is known to promote “coking”, i.e. carbon deposition, [7-9]. Consequently, nano-particles of NiO were used for the CCDL. The CCDL was designed so that it can be removed from the system if its catalytic activity decreases below a critical value where carbon deposition could occur on the cathode. The minimum catalytic activity required to avoid “coking” of the electrode will be determined in the proposed research. Once the CCDL is removed from the COG unit it can be regenerated. For example, on a Mars mission CO_2 from the Mars atmosphere could be used to gasify the carbon (the reverse Boudard reaction).

Electrolyte Design

Current COG technology, which uses YSZ electrolytes, must operate in the region of 700 - 1000 °C to avoid unacceptably high Ohmic losses. These high temperatures demand (a) heavy materials for fuel cell insulation and balance of plant, (b) significant energy input to heat up to the operating temperature. Moreover, since the human ambient temperature is ideally ~25 °C, it is critical to reduce the thermal gradient between the COG O_2 output and the ventilation loop gas temperature to achieve our goal of oxygen recovery and recycling. Therefore, if COGs could be designed to give a reasonable power output at lower temperatures tremendous benefits may be accrued. Lower operating temperature also results in: (i) reduced thermal stresses (e.g., from thermal expansion mismatches); (ii) lowered radiative losses ($\sim T^4$); and (iii) negligible electrode sintering. Alas, at lower temperatures the oxide ion conductivity of YSZ is too low for viable operation in a COG, Figure 4.

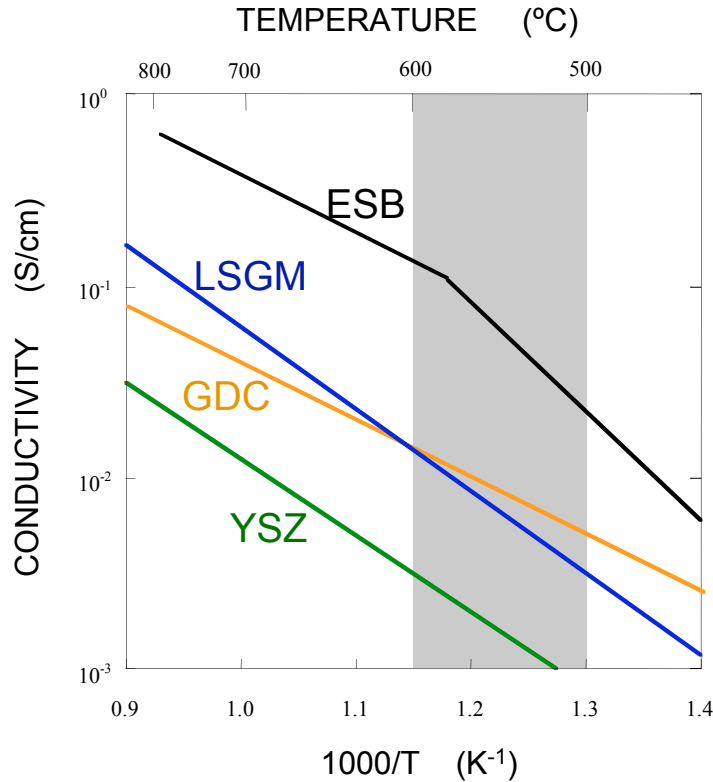


Figure 4. Comparison of the conductivity of candidate solid oxide electrolytes for SOFCs

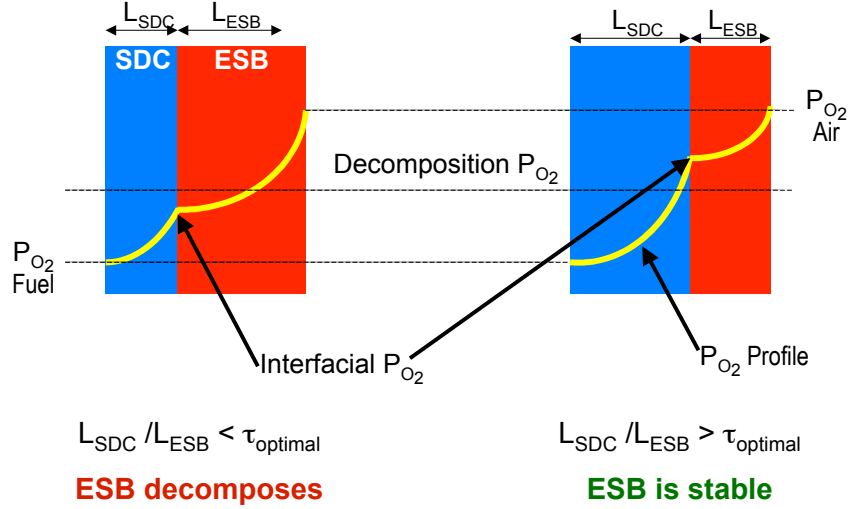


Figure 5. Conceptual illustration of a SDC-ESB bilayered electrolyte showing how the relative thickness can be varied to control the effective interfacial oxygen partial pressure (P_{O_2}) to protect the ESB from decomposition.

As shown in Figure 4, stabilized bismuth oxide (erbium-stabilized bismuth oxide, ESB, in the figure) and acceptor-doped ceria (gadolinia-doped ceria, GDC, in the figure) have the highest conductivity for the targeted temperature range of $\sim 500^\circ\text{C}$ and so should be good candidates for a low temperature COG electrolyte. However, in reducing conditions (i.e., high CO_2 reduction potential or low oxygen partial pressure) acceptor-doped ceria becomes a mixed conductor (thereby reducing its efficiency) and bismuth oxide decomposes. To overcome these problems we have developed and demonstrated a COG with a functionally graded bilayer electrolyte comprised of a layer of erbium-stabilized bismuth oxide (ESB) on the oxidizing side and a layer of samaria- or gadolinia-doped ceria (SDC or GDC) on the reducing side (since both have almost equal conductivity), as shown in Figure 5 [1, 2]. In this arrangement, if the constituent layers have the appropriate thickness ratio, the ceria layer is able to protect the bismuth oxide layer from decomposing by shielding it from very low oxygen partial pressures (P_{O_2} 's). Concomitantly, the ESB layer blocks electronic flux through the electrolyte and thereby neutralizes the efficiency sapping electronic leakage of the ceria layer. Thus, at worst, an SDC/ESB bilayer with a relatively thin layer of ESB should have the high conductivity of SDC but with improved efficiency due to the electronic flux barrier ESB provides. At best, the conductivity of the bilayer should approach that of ESB with a *relatively* thick layer of ESB.

EXPERIMENTAL

Catalytic Carbon Deposition Layer (CCDL)

To fabricate the CCDL, Nickel (Ni)-based catalysts were deposited on a ceramic tape that was first heat-cleaned to remove a protective coating and thus facilitate the adsorption of active metals on its surface. Two methods have been used for the Ni catalysts. In the first method, the heat-cleaned ceramic tape is dipped into a nickel nitrate solution. The nitrate solution is prepared by dissolving $\text{Ni}(\text{NO}_3)_2$ in deionized water. The ceramic tape is dried and then calcined (heated in air) at 450°C . The calcination in this case is done in air to decompose the nitrates and form

oxides, i.e. NiO. In the second method, nanoparticles of NiO (particle sizes: 20-30 nm) are dispersed in deionized water using ultrasonication. The resulting dispersion is then dripped onto heat-cleaned ceramic tape. The resulting catalysts are again dried and calcined at 450°C. The CCDL was then placed in a furnace in a range of temperatures and in a stream of CO gas to determine its capacity for carbon deposition.

Ceramic Oxygen Generator (COG)

Commercially available 10 mol% GDC (Anan Kasei) was used for the cathode support and electrolyte materials. In addition to GDC, either copper oxide (Alfa Aesar) or $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.50}\text{Mn}_{0.50}\text{O}_3$ (LSCM) were used in the cathode support. Erbium stabilized bismuth oxide was used in conjunction with the GDC for the bilayer electrolyte as well as with bismuth ruthenate for the anode.

LSCM was fabricated via a combined citrate and ethylenediaminetetraacetic acid (EDTA) complexing method [10, 11]. The LSCM was prepared by mixing stoichiometric amounts of metal nitrates in heated water to which EDTA-NH₃ and citric acid was added. The mixture was then heated in an oven at 80 °C until the water was evaporated. The resulting foam was heated to 250 °C for several hours then calcined in air at 800 °C for more than ten hours. This processed yielded a phase pure powder as determined by x-ray diffraction (XRD).

Erbium stabilized bismuth oxide (ESB) powder and bismuth ruthenate (BRO) powder was prepared by reacting stoichiometric amounts of the respective oxides. The ESB and BRO mixed oxides powders were milled in isopropanol overnight, dried, and then calcined for ten hours in air at 800 °C and 900 °C, respectively [12]. The BRO powders were leached with nitric acid prior to use in order to remove an impurity phase [13].

The cathode support was fabricated by tape casting mixtures of either 20 vol% CuO/GDC or 50 vol% LSCM/GDC. The tape casting slurry was composed of the ceramic powders, polyvinyl butyral binder, Solsperse (Noveon) dispersant, ethanol and toluene solvents, cellulose and graphite pore formers, and di-n-butyl phthalate binder lubricant. The mixtures were ball milled then cast on a heated bed. The cast tape was then rolled up into a hollow tube and capped at one end using the same tape, laminated to the same thickness as the tube wall. The resulting closed ended tube was slowly burned out and bisqued at 500°C for one hour.

A low solids loading GDC slurry composed of ethanol, binder, dispersant, lubricant, and 1 mol% iron nitrate, for increased sinterability, was used as the electrolyte coating slurry [14]. This slurry was poured into the tube then poured out three times then fired at 1000 °C for twelve hours to yield a dense, uniform GDC electrolyte and porous cathode support.

ESB was then coated on the inside of the tube by using a dilute slurry similar to the GDC coating slurry, but without iron. The coating was applied at least five times, thoroughly drying in-between the coats, and then densified at 900 °C for two hours. BRO was then coated onto the ESB using the same technique and fired at 800 °C for two hours to maintain porosity.

In the case of the CuO/GDC cathode supported tube, a 5.5M solution of copper nitrate with urea in a 1:1.5 copper:urea ratio was applied to the outside of the cathode support tube several times to create a continuous copper oxide phase [15]. This additional step minimizes mechanical stresses between the cathode support and electrolyte (from the thermal expansion

mismatch) incurred by increasing the CuO content in the cathode. The LSCM/GDC composite needed no addition since both phases percolate as prepared.

Silver mesh was used as the electrodes on both the outside and inside of the COG tube. The mesh was adhered to the tube using platinum paste. Silver leads were used inside the furnace for current transport to the electrodes. The CCDL was wrapped around the cathode support, surrounding the cathode electrode. The tube was then fitted into an apparatus that allowed CO/CO₂ to flow on the outside (cathode) and inert sweep gas to flow through the inside (anode) as shown in Figure 7. The oxygen was pumped to the anode using a large DC power supply and measured in the effluent sweep gas using a gas chromatograph.

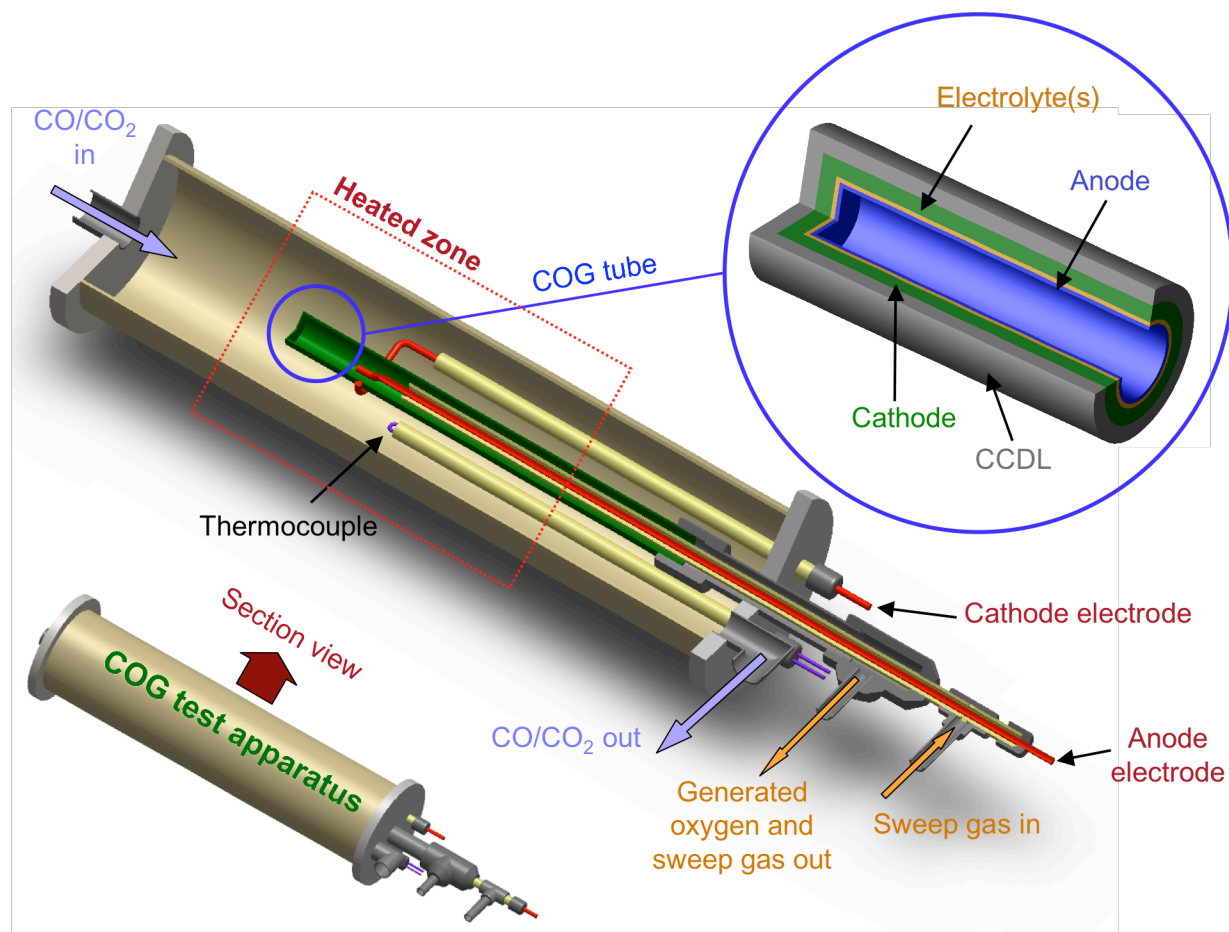


Figure 6. Illustration of the COG/CCDL test apparatus.

RESULTS AND DISCUSSION

Catalytic Carbon Deposition Layer (CCDL)

A CCDL was fabricated and tested. Figure 7 shows pictures of the CCDL before it was exposed to CO gas at 600 °C. As can be seen there was significant carbon deposition. Several Ni catalysts supported on ceramic tape prepared via the nitrate method were tested for the CO decomposition reaction at different temperatures; 450°C, 550°C and 650°C to see if the carbon deposition could be maximized (the carbon deposition is thermodynamically favored at lower temperatures, however it is kinetically favored at the higher temperatures). There was no significant difference in the carbon deposition on these catalysts at any of the temperatures probed.

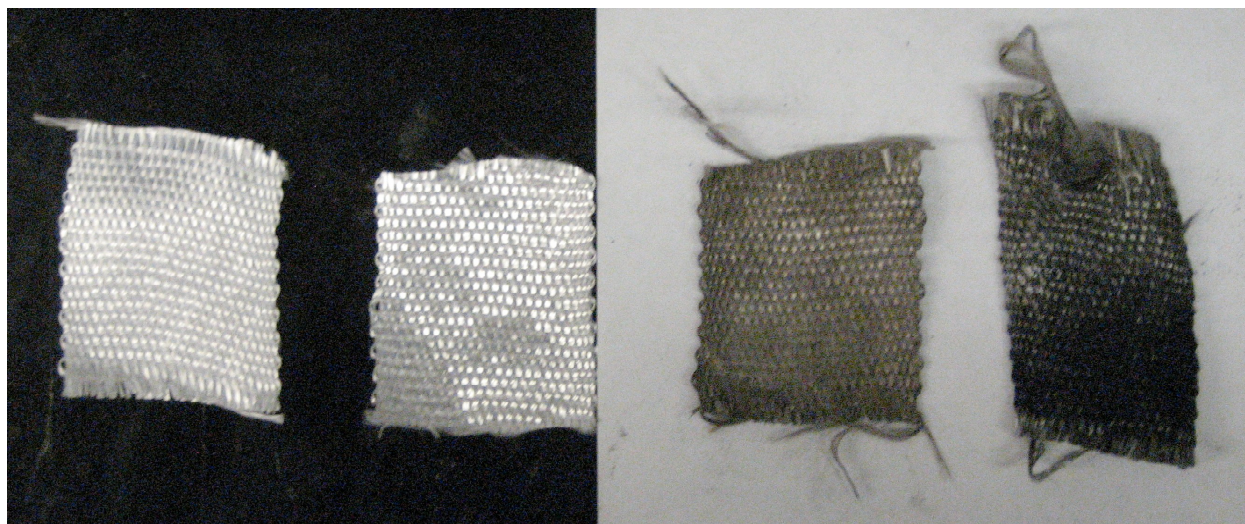


Figure 7. (a) Catalytic carbon deposition layer (with Ni catalysts supported on ceramic tape) before exposure to CO (b) CCDL after exposure to CO at 650°C.

Ceramic Oxygen Generator (COG)

An electronically and ionically conductive copper-ceria cermet cathode (good electronic conduction is crucial for current collection and oxygen exchange) was developed, Figure 8. The cathode resistance was found to be $< 0.1 \text{ ohm/cm}$, Figure 8. However, CuO (used in fabricating the Cu-ceria cermet) content must be optimized to minimize the stress buildup (due to thermal expansion mismatches) between electrolyte and cathode support (which results in crack formation, Figure 9), while maintaining good electronic conductivity.

Figure 9 shows an SEM (scanning electron micrograph) of the COG cross-section. In the figure we see the dense bilayer electrolyte (GDC/ESB) sandwiched by porous electrodes (CuO/GDC cathode and BRO/ESB anode).

At present our preliminary performance results are not ready for publication as we have not completed our repeatability studies. Nevertheless, results obtained from earlier COG work

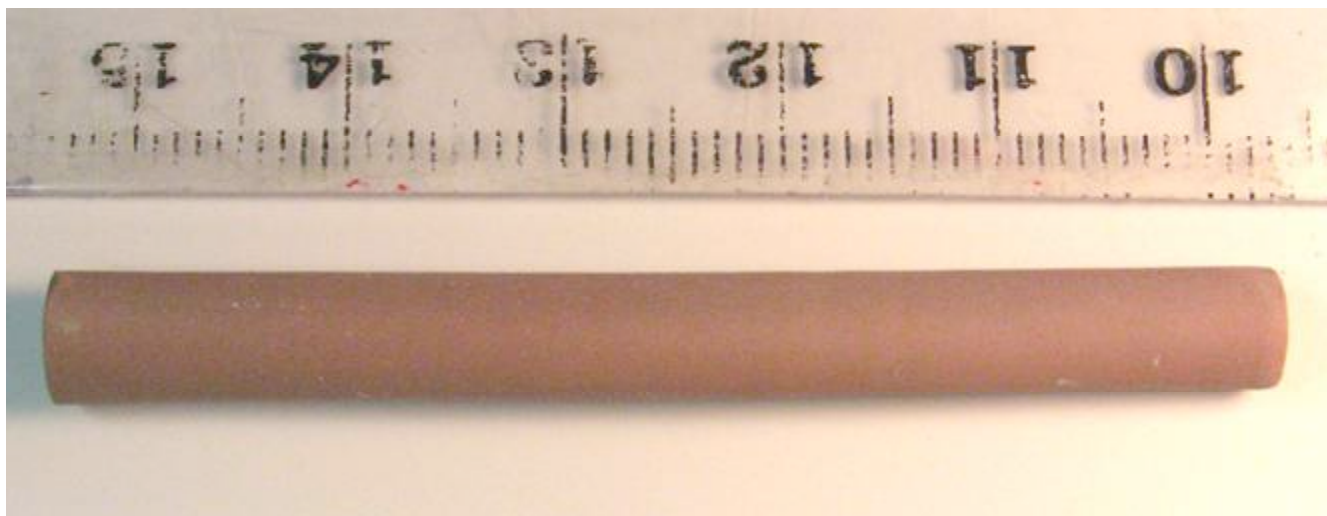


Figure 8. Cu-GDC cermet cathode sintered 1100 °C for ten hours and then reduced at 800 °C for ten hours in Ar/H₂/H₂O (oxygen partial pressure $\sim 10^{-19}$ atm) yielding a resistance < 0.1 ohm/cm.

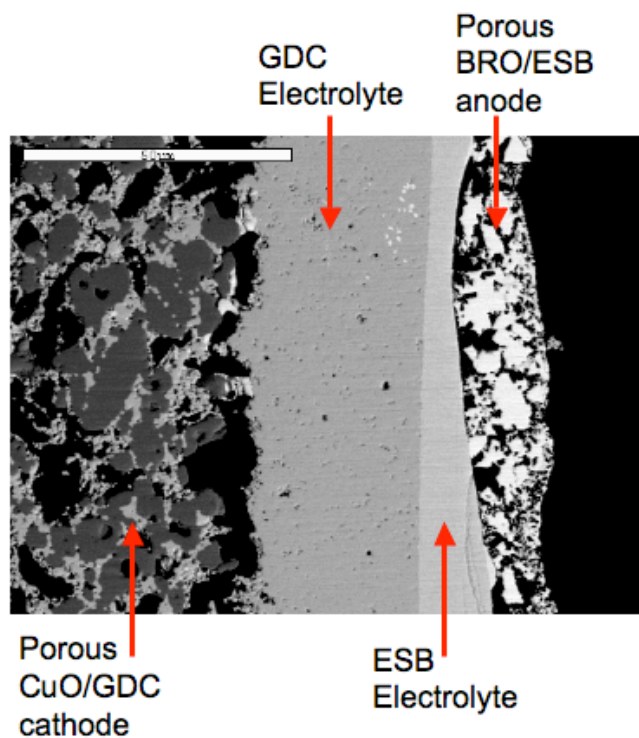


Figure 9. Scanning electron micrograph showing cross-section of a ceramic oxygen generator with porous CuO/GDC composite cathode, dense GDC electrolyte layer, thin dense ESB (electron blocking) electrolyte layer and porous BRO/ESB composite anode.

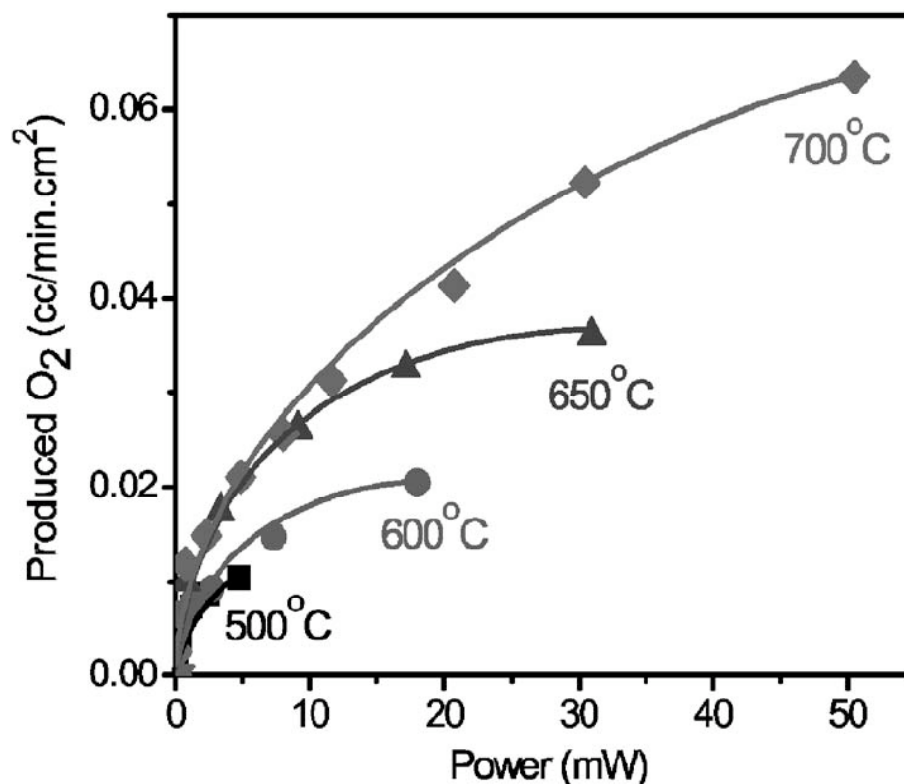


Figure 10. Oxygen flux produced from CO as a function of applied power.

with a thick (~1.5 mm) electrolyte are given in Figure 10 which shows the power requirement for oxygen generation at different temperatures. Power (which is the product of cell voltage and applied current) is consumed in several ways during the oxygen generation process. These power losses may be represented as effective resistances within the COGs and include ohmic resistance due to electron or ion conduction, the electrochemical effective resistance caused by the transfer of oxygen across the electrode/electrolyte interface and contact resistance at the interface of the electrode/electrolyte. Our present COG has a thickness of ~40 μm and has superior electrodes so we anticipate, conservatively, at least a 30-fold increase in performance.

CONCLUSION

A concurrent O_2 generation and CO_2 control system for advanced life support was developed. The system consists of a novel high oxide ion conductivity electrolyte suitable for low temperature operation, a removable catalytic carbon deposition layer (CCDL) to promote full CO_2 reduction while avoiding the problem of “coking”, and a pre-stage for CO_2 absorption to concentrate CO_2 from the exhalate before sending it to the COG. Based on earlier work, the device specifications are promising (thinner electrolyte, improved electrodes and CCDL), and performance tests are currently being completed.

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